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**SYNTHESIS OF NANOSTRUCTURED LiCoO₂
AS CATHODE MATERIAL FOR LITHIUM-ION BATTERIES**Y.Y.Mamyrbaeva^{1,2}, M.A. Hobosyan¹, S.E. Kumekov², K.S. Martirosyan¹¹University of Texas at Brownsville, Department of Physics and Astronomy, Brownsville, TX, 78520, USA²Kazakh National Technical University named after K.I. Satpaev, Almaty, Kazakhstan

Nanostructured LiCoO₂ powders were prepared by Carbon combustion synthesis of oxide method using carbon as starting materials. The thermo-gravimetric analysis was used to identify interaction features in the system LiNO₃ - Co₃O₄ – Carbon to produce LiCoO₂. X-ray diffraction showed that the as-synthesised product were single phase. The crystalline nanoparticles synthesized were nearly spherical, and their average particle diameters ranged from 60 to 200 nm. Cyclic voltammetry and charge-discharge experiments were applied to characterize the electrochemical properties of the powders as cathode materials for lithium-ion batteries. The cyclic voltammogram curves indicated faster diffusion and migration of Li⁺ cations in the nanostructured LiCoO₂ electrode. In the first charge-discharge process, the material showed the capacity of 200 (mAh)/g.

Keywords: Carbon Combustion Synthesis of Oxide (CCSO), Lithium Cobaltate, Nanoparticles, Li-ion Rechargeable Batteries.

INTRODUCTION

There are different sources for energy, and they vary from one country to another, but globally it is based on fossil fuel. There are many challenges associated with the use of fossil fuels (oil, coal, and gas), most important of which is the release of greenhouse gasses, mainly CO₂, that are responsible the devastating effects of raising the Earth's temperature in what has become known as global warming. Also, fossil fuels are finite and nonrenewable source of energy. Currently, it is urgent to find alternative energy sources to replace. This can be achieved by increasing energy efficiency and conservation of processes while utilizing current energy sources. However, it could be more effective by adopting less-polluting, less-harmful, and abundant alternative energy sources such as solar, wind, ocean and hydroelectric. Energy can be converted from one form to another and can also be stored in different forms. Electrochemical devices such as batteries are one popular form of storing electricity in the form of chemical energy and reverse the process by converting the chemical energy to electricity. Current demand for lithium batteries is conquered by the compact electronics and power tool industries, but emerging automotive applications such as plug-in hybrid electric vehicles or pure electric vehicles are now appealing. The lithium ion battery is used as a main electrical storage to power electric vehicle and hybrid vehicle. Also, with the invention of high energy density batteries, very large systems can be used to facilitate a more efficient transmission and delivery of electricity by the grid and its integration with solar and wind energy sources [1].

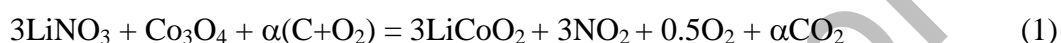
In addition, the main challenge in high-rate charge discharge experiments is kinetic problems due to the slow diffusion of Li-ions in the electrodes. Decreasing the particle size to the nanoscale domain is a best solution to achieve a higher surface area of electrode to shorter Li-ion diffusion length for increasing mobility. It is not only enhancing the performance of the batteries but also extends some materials electrochemical activity. There is an increased contact area between the electrode and the electrolyte that leads to better charge and discharge rates. The volume changes originating from Li⁺ insertion/desertion will be better accommodated by nanomaterials compared to microscale materials due to faster stress relaxation, which can extend the battery cycle life [1-6].

In this paper we have tested a novel method calls for Carbon Combustion Synthesis of Oxides (CCSO) to rapidly produce high-purity, nanoscale powders of lithium cobaltate (LiCoO₂). It is a

modified form of self-propagating high temperature synthesis (SHS) that uses carbon as the fuel instead of a pure metal. CCSO has several advantages over SHS especially it is a more economical synthesis of complex oxides. In CCSO the extensive emission of CO_2 affects the product structure, changes the local thermal physical properties (such as heat capacity and conductivity) and causes a loss of heat to the surrounding. The high rate of CO_2 release helps form a highly porous (up to 70 %) and friable product, having a particle size in range 50-800 nm with a surface area up to $10 \text{ m}^2/\text{g}$. It was reported fabrication by CCSO homogeneous, nanostructured complex oxides such as BaTiO_3 , LaGaO_3 [7-10].

EXPERIMENTAL RESEARCH

The LiCoO_2 were produced by CCSO via the reaction:



A self-sustaining reaction could not be attained when the carbon wt. % in the reactants mixture was smaller than 6. The combustion proceeded in an unstable mode at $x=7-7.5$ wt. % and the front extinguished after moving for about 3-5 mm. A stable front motion generated using 8-20 wt. % of carbon led to maximum temperatures of 600-1100 °C below the melting temperature of the LiCoO_2 .

For the synthesis of LiCoO_2 , we used LiNO_3 (99 %, Sigma Aldrich), Co_3O_4 (99.5 %, Sigma Aldrich) and Carbon (particle size < 50 nm, 99 %, Sigma Aldrich). The molar ratio among the reactants was set according to the stoichiometry of the desired product. The reactants were thoroughly mixed with carbon powder ("carbon acetylene") by ball milling for about 60 min. The combustion synthesis was conducted by loading a loose mixture (relative densities of about 0.3) into a ceramic boat that was placed inside a cylindrical stainless steel vessel (30- mm i.d. and 50- mm length) fed by oxygen at a flow rate at 20 ml/min. To initiate the propagating temperature front the reactant mixture was locally ignited by an electrically heated coil. The local combustion temperature (T_c) was measured by inserting in the center of the sample an S-type (Pt-Rh) micro thermocouple of 0.1 mm diameter. The thermocouple readings were recorded and processed by an Omega data acquisition board connected to a PC.

The Differential Scanning Calorimetry (DSC) (Q-600, TA Instrument) was used to test $\text{LiNO}_3\text{-Co}_3\text{O}_4\text{-C}$ reactions with linear heating rate 20 °C/min, with resolution of mass changes of 0.1 microgram, which provides opportunity to work with very small amounts of mixtures (~20 mg). The DSC experiments were conducted under air. The composition and crystal structure of the products was determined by X-ray diffraction (XRD; Siemens D 5000 diffractometer) with Cu-radiation.

RESULTS AND DISCUSSION

Synthesis of lithium cobaltate

To understand details of the reaction that is occurred during the CCSO of LiCoO_2 we conducted differential scanning calorimetry experiments using following systems $\text{LiNO}_3\text{-Co}_3\text{O}_4$ and $\text{LiNO}_3\text{-Co}_3\text{O}_4\text{-C}$. To initiate exothermic reaction, we added 10 wt. % of Carbon to the initial mixture. To utilize the oxygen releasing from the LiNO_3 decomposition we need at least 8.5 wt. % Carbon in initial mixture, if we assume that carbon is reacting with oxygen giving carbon dioxide CO_2 . By Differential Scanning Calorimetry was established that due to presence of nanostructured carbon, the decomposition of LiNO_3 is occurring. This indicates that Carbon is readily reacting with the oxygen released from LiNO_3 decomposition. After each the weight loss was increased which is due to excess amount of carbon that we have in the system.

The XRD patterns of the sample at different heating temperatures were applied to track the formation of LiCoO_2 which are illustrated on the Figure 1. The addition of carbon to the initial

mixture of $3\text{LiNO}_3\text{-Co}_3\text{O}_4$ is transforming the system from endothermic to exothermic interaction, which shows all the major diffraction peaks for as-synthesized powders were corresponding to lithium cobaltate oxide. This is implying that the heat released from carbon combustion assists the formation of the layered structure. The lack of diffraction patterns of other species indicates that the concentrations of any other crystalline species must be very low.

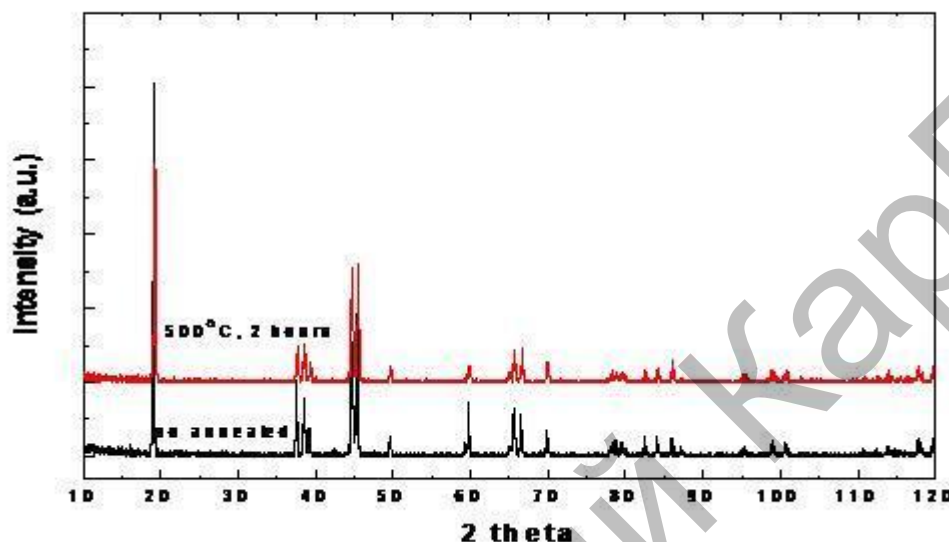


Fig.1. X-ray diffraction patterns of lithium cobaltate oxide (LiCoO_2): (black)- produced by CCSO, (red) - after the calcinations of the as-synthesized product at $500\text{ }^\circ\text{C}$ for 2 h

Charge-discharge study

Figure 2 shows the cyclic charge-discharge voltage-current-time recordings for the first 5 cycles of the battery with LiCoO_2 prepared at $800\text{ }^\circ\text{C}$ at 10wt.% content of carbon. In order to study the multiple charging-discharging influence on the performance of Li-ion battery made with the synthesized LiCoO_2 as cathode material, the battery was tested over 30 cycles and the current, voltage, capacity and charging-discharging efficiency curves were monitored during the measurement process. In the first stage, the battery was charged with 150 mA/h constant current mode until the voltage raised to 4.2 V.

At this point, the charging mode shifted to 4.2 V constant voltage charging mode and charging continued until the current dropped to the 10 % of initial value (15 mA/h). After charging, the battery was relaxed for 1 min and then the constant current discharge with 50 mA/h was applied until the voltage dropped to the cutoff value of 2.7 V. After another 1 minute rest, the cycle repeated from the constant voltage charging mode. The duration of one cycle was about 2 hours.

Figure 3 is presenting the time dependence of recorded voltage over 30 cycles. The cycle curves are advancing from the right to the left. Thus, the longest cycle was the first cycle with 105 minute overall duration (38 min charging and 67 min discharging), whereas the last cycle duration was 75 minute (20 minute charging and 55 minute discharging). The decreasing tendency of charge-discharge time of one cycle is indicating that the battery capacitance is also decreasing because initially more Li ions could pass from cathode to anode and vice versa, but after several cycles not all ions are returning to their initial positions and therefore the capacitance is dropping over many cycles, which is a known factor for the rechargeable batteries. However, seemingly significant time decrease of charge-discharge cycle is not indicating significant capacity loss as can be seen from the Figure 3.

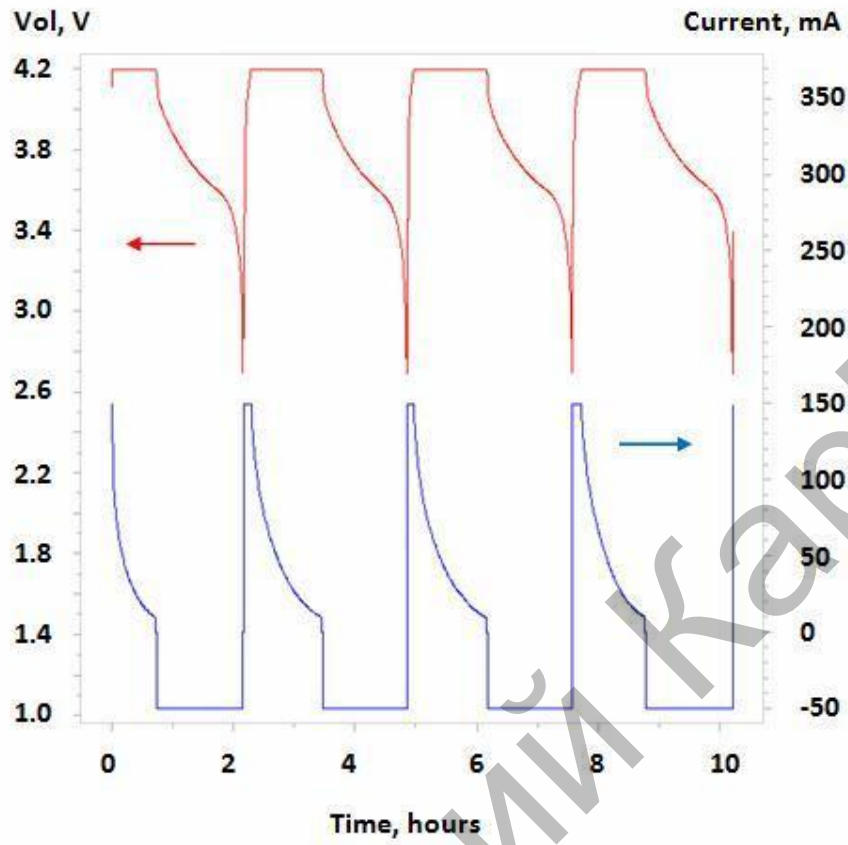


Fig.2. The cyclic charge-discharge voltage-current-time recordings for the first 5 cycles by using lithium cobaltate produced by CCSO

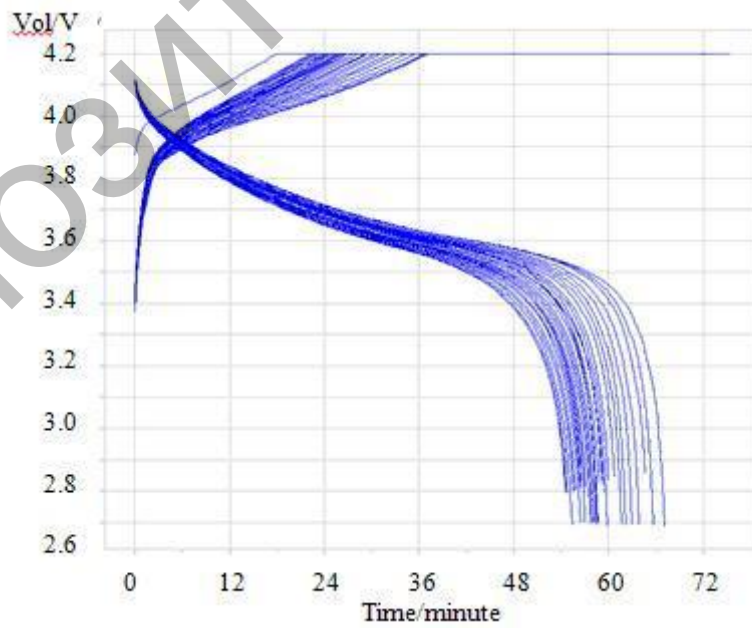


Figure 3. The charge-discharge voltage time evolution during first 30 cycles

The efficiency is indicating how complete was performed the current cycle run compared to the previous cycle. Thus, the efficiency of less than 100 % is indicating that the cycle under consideration showed less capacity compared to previous cycle, whereas efficiency more than 100 % is showing that the current run was showing better capacity value than the previous cycle. The small deviations around 100 % of efficiency is showing that the cycles showed substantial consistency over 30 cycles. The specific capacity had initial value of 200 mAh/g and after 30 cycles the capacity dropped to almost 180 mAh/g showing that over 90 % of initial capacity is preserved over continuous charge-discharge series. This result is confirming that CCSO synthesized ultrafine LiCoO₂ has stable structure and gives opportunity to extract more than 66 % of theoretical capacitance (200 mAh/g from theoretical value of 300 mAh/g) [11,12].

CONCLUSIONS

In this paper, a carbon combustion synthesis method was used to prepare LiCoO₂ for lithium ion batteries. The particles size increase with increasing carbon content. The sample prepared at 800°C with 10wt.% carbon content has better electrochemical performance than other samples. XRD analysis shows that as-synthesized powder was single phase as lithium cobaltate. The results are well comparable to best commercial cathode powders, showing available capacity of about 200 mAh/g.

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